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INVESTIGATION ON HYDROGEN BONDING IN PURE CHLORO- AND NITRO ANILINES AND THEIR SOLUTIONS IN POLAR SOLVENTS

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ABSTRACT The changes in the frequencies of infrared absorption bands due to N-H stretching vibrations in pure ortho-, meta-, para-chloro- and nitro aniline and in their solutions in different polar solvents with respect to the values in solutions in carbon tetrachloride have been measured. It has been observed that the reduction in the N-H stretching force constant in different solvents with respect to its value in carbon tetrachloride solution bears a linear relationship with the sum of the shifts of the two frequencies. It has been found that there is no systematic dependence of the total shifts either on the dielectric constants of the solvents or on the dipole moments of the molecules of the solvents

INTRODUCTION

Recently, Krueger (1962) has elaborately discussed the variations of the N-H stretching force constant and the interbond HNH angle of the NH_2 group of a large number of substituted anilines in solution in carbon tetrachloride with the variation of the Hammett σ-factor of the substituent atom or group of atoms and also with the state of hybridisation of the N-H bonds. Earlier, Bryson and Werner (1960) had shown that information regarding the existence of intramolecular hydrogen bonds in some nitrosubstituted anilines and naphthylamines can be obtained from a study on the change in the N-H stretching force constant of the NH_2 group in the molecules of these compounds with a change of the solvent from carbon tetrachloride to pyridine. More recently, Medhi and Kastha (1963) have concluded that the shifts in the N-H stretching frequencies of aniline and a number of methoxy-and ethoxy-anilines in the liquid state and in solution in some polar solvents relative to the frequencies in solutions in dilute carbon tetrachloride depend on the electronic nature in substituent groups, the relative positions of substitution and on the nature of the solvents. In the present work the investigation has been extended to the chloro- and nitro- derivatives of aniline and the results obtained have been discussed in the following paragraphs.

EXPERIMENTAL

The substances investigated are *o*-, *m*- and *p*-chloroaniline and *o*-, *m*- and *p*-nitroanilines. Chemically pure samples of these compounds were obtained

from reputed firms of U.K. and West Germany. The chloroanilines were fractionated and the solid samples of the nitroanilines were crystallised from suitable solvents. All the compounds were then distilled under reduced pressure. The solvents used were purified and carefully dried. The infrared absorption spectra of the pure compounds and their solutions in different solvents were recorded on a Perkin-Elmer Model 21 double beam instrument provided with rock salt optics under conditions described in an earlier paper (Banerjee and Kastha, 1962). In order to complete the investigation infrared absorption in nitroanilines in the solid state at the room temperature was also studied. The melting point of the nitroanilines being high, the spectra of the melts of these compounds could not be recorded, and instead, the spectra due to the compounds mulled in paraffin oil were obtained. The absorption bands due to N-H stretching vibrational frequencies of aniline in dilute solution in carbon tetrachloride were recorded from time to time throughout the investigation to check the reproducibility of the recorded spectra.

RESULTS AND DISCUSSION

The symmetric and asymmetric N-H stretching vibrational frequencies in cm^{-1} (denoted by ν_s and ν_a respectively) of the pure compounds and of their solutions in different solvents are given in Table I. The values of the sum of the shifts in the N-H vibrational frequencies in cm^{-1} $(\Delta\nu_s+\Delta\nu_a)$ of each of the compounds in the different environments relative to the frequencies of the compound in dilute solution in carbon tetrachloride have been entered in Table II which also contains some data obtained in previous investigations for the sake of comparison. The Hammett σ-factors for the various substituents and the pK_a values of the bases, all taken from a paper of Whetsel (1961) have been included in both the Tables.

It is seen from Table I that the N-H stretching frequencies of the pure compounds and of their solutions in polar solvents are lower than those of the respective compounds in solution in carbon tetrachloride. This lowering of the vibrational frequencies is attributable to the formation of intermolecular hydrogen bonds as suggested in an earlier paper (Medhi and Kastha, 1963), If the N-H bonds are not greatly weakened due to the formation of the hydrogen bonds, the decrease in the N-H stretching force constant in dynes cm^{-1} is approximately given by $\Delta f = 5.52\times10^{-2}(\nu_s\Delta\nu_s+\nu_a\Delta\nu_a)$ where ν_s and ν_a are the vibrational frequencies in cm^{-1} of the molecule in solution in carbon tetrachloride and $\Delta\nu_s$ and $\Delta\nu_a$ denote respectively the decrease in the values of the symmetric and asymmetric frequencies in passing from CCl_4 solution to the medium in which hydrogen bonding takes place. Remembering that $\nu_a \simeq \nu_s(1+\delta)$ where δ is a small fraction and that $\nu_s \simeq 3400$ cm^{-1}, we find $\Delta f \simeq 188(\Delta\nu_s+\Delta\nu_a)$ This shows that to a first approximation the reduction in the value of the N-H stretching force constant is proportional to the sum of the shifts in the two N-H stretching fre-

quencies. The values of the N-H stretching force constant of the compounds in the liquid state and in solution in carbon tetrachloride and the polar solvents have been calculated and the decrease in the force constant (Δf) with respect to that of the respective compounds in solution in CCl_4 has been obtained in

TABLE I

N-H stretching frequencies ν_s and ν_a in cm^{-1}

Name of the compound and Hammett σ pK_a	Pure		Solution in					
	Solid	Liquid	CCl_4	$CHCl_3$	$(CH_3)_2CO(C_2H_5)_2O$		$(CH_2)_4O$	C_6H_5N
o-Chloro aniline		3380	3406	3400	3379	3367	3358	3330
.....								
2 79		3453	3485	3480	3444	3462	3445	3442
m-Chloro aniline		3373	3408	3400	3383	3372	3362	3340
0 373								
3.52		3438	3485	3473	3443	3450	3436	3430
p-Chloro aniline		3380	3405	3403	3383	3377	3365	3342
0 227								
4.05		3443	3480	3468	3449	3450	3430	3439
o-Nitro aniline	3337		3410	3410	3372	3360	3340	3305
.....								
—0.05	3465		3520	3516	3482	3480	3474	3465
m-Nitro aniline	3319		3411	3411	3386	3377	3368	3344
0.710								
2.52	3406		3493	3493	3457	3462	3433	3345
p-Nitro aniline	3360		3421	3420	3384	3370	3360	3340
1.270								
0.99	3478		3503	3505	3455	3443	3428	3467
Aniline		3360	3402	3398	3380	3376	3364	3340
0.00								
4.68		3420	3476	3460	3450	3448	3438	3430

TABLE II

Total shift in N-H stretching frequencies ($\Delta\nu_s + \Delta\nu_a$) in cm^{-1}

Compound Hammett σ pK_a	Pure		Solution in				
	Solid	Liquid	$CHCl_3$	$(CH_3)_2CO$	$(C_2H_5)_2O$	$(CH_2)_4O$	C_5H_5N
o-Chloro aniline 2.79		58	11	68	62	88	119
m-Chloro aniline 0.373 3 52		82	20	67	71	95	123
p-Chloro aniline 0.227 4 05		62	14	53	58	90	104
o-Nitro aniline .... −0.05	128		4	76	90	116	160
m-Nitro aniline 0.710 2 52	179		0	61	65	103	115
p-Nitro aniline 1 27 0 99	86		−1	85	111	136	117
Aniline 0.00 4 68		98	20	48	54	76	108
o-Anisidine 4 59		53	32	46	35	55	117
m-Anisidine 0 115 4.32		75	24	51	54	76	108
p-Anisidine −0 268 5.40	162	82	32	40	49	54	88
o-Phenetidine .. 4.47		62	38	51	40	66	123
m-Phenetidine 0 150 4.17		80	29	50	58	77	108
o-Toluidine ... 4.53		59	24	45	42	76	86
m-Toluidine −0.069 4.81		78	27	36	45	75	80
p Toluidine −0.170 5.15	86	74	33	52	55	78	82

each case. The plots of the total shifts ($\Delta\nu_s+\Delta\nu_a$) against Δf for some of the compounds shown in Figs. 1(a) and 1(b) are found to be straight lines, as expected.

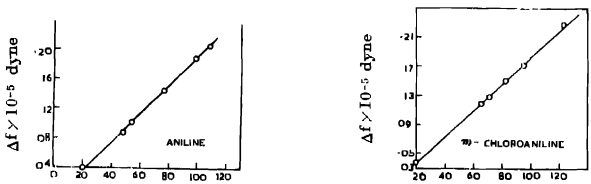


Fig. 1. Relation between the total solvent shifts ($\Delta\nu_s+\Delta\nu_a$) in cm^{-1} and decrease in N–H stretching force constant (Δf) of (a) aniline, (b) m-chloroaniline.

In a previous paper (Medhi and Kastha, 1963) it has been pointed out that the plots of the mean solvent shifts i.e., $\frac{1}{2}(\Delta\nu_s+\Delta\nu_a)$ of aniline in different environments against the corresponding quantities for some substituted anilines under similar conditions are straight lines with slopes different for the different compounds. In the present investigation similar graphs have been plotted for the compounds studied and some of them are shown in Figs. 2(a), (b) and (c). All the graphs are straight lines having different slopes. The values of the

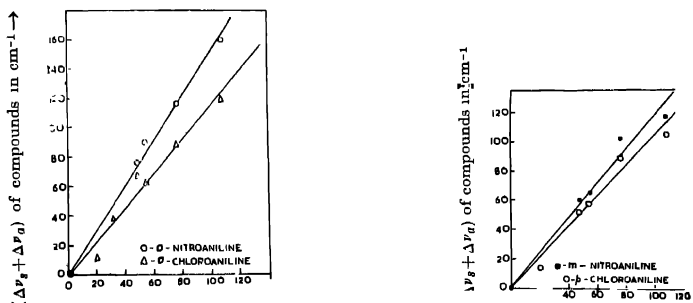
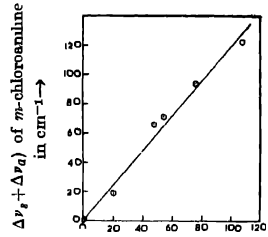


Fig 2. Plot of total solvent shifts ($\Delta\nu_s+\Delta\nu_a$) in cm^{-1} of
(a) o-nitroaniline and o-chloroaniline (b) m-nitroaniline and p-chloroaniline

slopes (denoted by S) obtained in the present investigation and also from data due to compounds investigated earlier, have been plotted against the corresponding pK_a values of the bases in Fig. 3 and the two quantities are found to be linearly related. This indicates that the S-values of the compounds may be taken as a measure of their pK_a values i.e, the proton donating capacities of the different bases with respect to aniline itself.



$(\Delta\nu_s+\Delta\nu_a)$ of aniline in cm^{-1}

Fig. 2(c). Plot of total solvent shifts $(\Delta\nu_s+\Delta\nu_a)$ in cm^{-1} of *m*-Chloroaniline against those of aniline

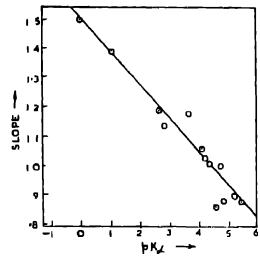


Fig 3. Dependence of slopes (S) of pK_a values of compounds.

It is seen from Table II that in the case of the solution of the compounds in chloroform, the total solvent shifts for compounds having negative σ-values are greater while for compounds which have positive σ-factors the shifts are smaller than that for aniline. This may be due to the fact that for positive σ-factor, the positive charge on the N-atom of the NH_2 group in the molecules increases and consequently the strength of the hydrogen bonds formed between the N-atom and the hydrogen atom of the solvent molecule (cf. Moritz, 1961 ; Whetsel, 1961) decreases.

The situation, on the otherhand, is just the reverse in the cases of proton-acceptor solvents such as, acetone, ether, tetrahydrofuran and pyridine. For any of the aniline compounds, the shifts are largest in the case of its solution in pyridine and of the three isomers of a given compound the lowering in the N-H frequencies due to a change of the solvent from CCl_4 to pyridine is maximum for the ortho-isomer. This fact is in disagreement with the results reported by Bryson and Werner (1960). This discrepancy may be due to incorrect values of the two N-H frequencies due to the meta- and para-nitro anilines used by them.

It is observed that for aniline and substituted meta- and para-compounds of aniline the magnitude of the solvent shifts increases as the solvent is changed

successively from acetone to ether, tetrahydrofuran and pyridine. The ortho-compounds, however, behave differently, the shifts in solution in ether being less than that in solution in acetone. This may be due to the steric effect as suggested earlier (Medhi and Kastha, 1963).

The effect of steric hindrance on the strength of intermolecular hydrogen bonds is also discernible from an examination of the data on shifts in the N-H frequencies of some of the pure aniline compounds in the liquid state with respect to the values for the solutions in CCl_4 as given in Table II. It is seen that the shifts for the ortho-compounds are less than those for the meta- and para-compounds. However, in all the cases the total shifts are less than that observed in the case of the parent compound aniline, which probably indicates that the relative charge difference on the N-atom and the H-atom in the virtual bond of the N-H. . . . N bridge is less in the substituted anilines than in aniline itself.

Finally, it would be of interest to find out whether there is any systematic dependence of the total solvent shifts in the various polar solvents on the dielectric constant of the solvents and on the dipole moments of their molecules. For this purpose the data have been collected from Landolt-Börnstein and International Critical Tables and are given in Table III.

TABLE III

Solvent	Chloroform	Acetone	Ether	Tetrahydro furan	Pyridine
Dipole moment in Debye unit	1 10	2 71	1.04	1 71	2.26
Dielectric constant	5 05	21 40	1 335	—	12 5
Solvent shift of aniline in cm^{-1}	20	48	54	76	108

It is seen from the table that there is no systematic relation between the total solvent shifts and the values of the two constants.

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